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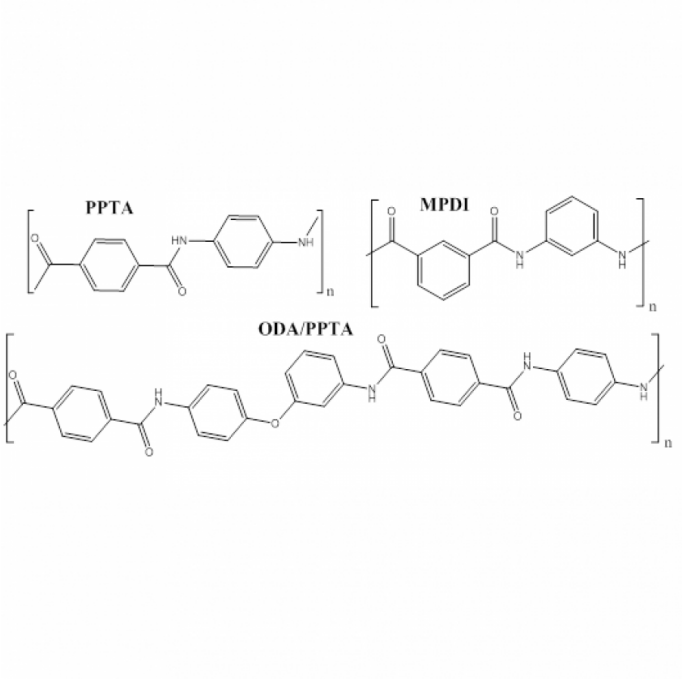
Ionic liquids as solvents for polyaramids

AUTHORS
Jonas WINTERS / KULEUVEN, MOLECULAR DESIGN AND SYNTHESIS, CELESTIJNLAAN 200F, LEUVEN
Koen BINNEMANS / KULEUVEN, MOLECULAR DESIGN AND SYNTHESIS, CELESTIJNLAAN 200F, LEUVEN
Wim DEHAEN / KULEUVEN, MOLECULAR DESIGN AND SYNTHESIS, CELESTIJNLAAN 200F, LEUVEN

PURPOSE OF THE ABSTRACT

Ionic liquids are solvents made up entirely out of ions, with a melting point below an arbitrary temperature of 100 °C. They have several desirable properties such as high thermal stability, high liquidus range, low flammability and a negligible vapor pressure. Furthermore they are very strong solvents, being able to dissolve materials such as cellulose or kerogen. Because of this, ionic liquids can be suitable candidates for the replacement of volatile organic compounds (VOCs) in many applications. Polyaramids (aromatic polyamides) are known as a class of high performance polymers. Their high mechanical strength and heat resistance allow these materials to be used for many applications such as protective clothing, ballistic protection, material reinforcements, etc. Important aramid products are poly(para-phenylene-terephthalamide) (PPTA), poly(meta-phenylene-isophthalamide) (MPIA) and copoly(3,4?-diphenylether/para-phenylene-terephthalamide) (ODA/PPTA). These products are used in the production of well-known fibers such as Kevlar® and Twaron® (PPTA), Nomex® and Teijinconex® (MPDI) and Technora® (ODA/PPTA). Polyaramids owe their superior properties to the rigidity of the aromatic backbone, the inertia of the amide bonds, and their ability to use the amide functionalities to form a network of intermolecular hydrogen bonds. However, due to this network of hydrogen bonds, polyaramids have very low solubilities in classical organic solvents. The state-of-the-art industrial polymerization processes utilize a mixture of an amide solvent such as N-methyl-2-pyrrolidone (NMP) or dimethylacetamide (DMA) mixed with an inorganic salt such as CaCl2. The chloride anions interact with the N-H hydrogens of amide bonds and thus interrupt the intermolecular hydrogen bonds, rendering the polymer soluble. For processing, this type of solvent is not suitable and a strongly acidic solvent, such as concentrated sulfuric acid is required. NMP and DMA are suspected reproductive toxins and have been placed on a Substance of Very High Concern (SVHC) list in 2011 and 2012 respectively. Their use might be subject to restrictions and regulations in the near future.
Ionic liquids could be more benign alternative solvents for polyaramids. Their application in the dissolution and processing of cellulose is already well understood. The intermolecular hydrogen bond network of cellulose is broken up by the ionic moieties. This is comparable to the dissolution mechanism of polyaramids in solvent systems such as NMP/CaCl2. Earlier work has already shown that ionic liquids are capable of dissolving PPTA pentamer model compound, and they show potential as synthesis media for PPTA[1]. This work has been expanded to the meta-polyaramid MPIA. Solubility tests were performed using a series of ionic liquids, and the dissolution mechanism was studied using FTIR and NMR spectroscopy. It was found that MPIA shows a much greater solubility in ionic liquids than PPTA. Furthermore it was found that several ionic liquids were successful for dissolving PPTA, were poor solvents for MPIA and vice versa.

FIGURES



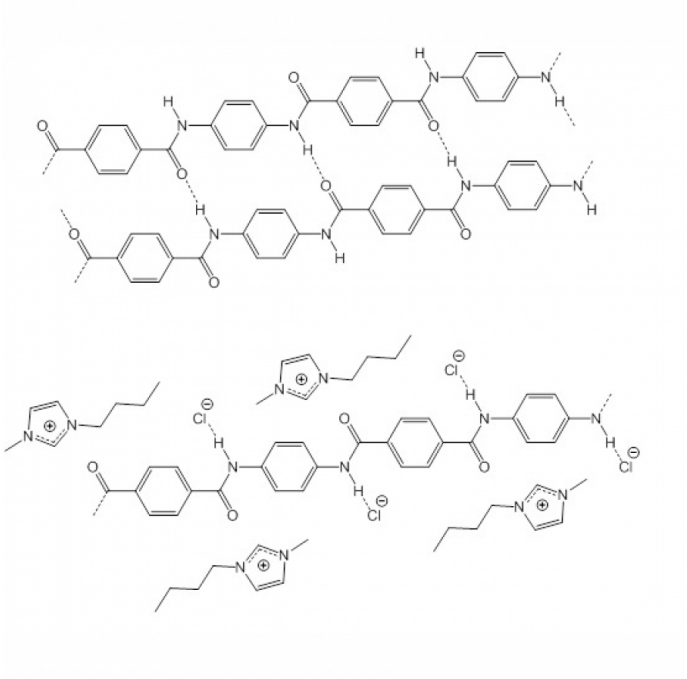


FIGURE 1

Figure 1

Chemical structures of the polyaramids PPTA, MPDI and ODA/PPTA

FIGURE 2

Figure 2

Top: hydrogen bond network in PPTA. Bottom: postulated mechanism for the dissolution of PPTA in ionic liquids

KEYWORDS

Polyaramid | Ionic liquids | Hydrogen bond | N-methylpyrrolidone

BIBLIOGRAPHY

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